Conductometric Study of Complex Formation Between Cu(II) Ion and 4-Amino-3-ethyl-1,2,4- triazol-5-thione in Binary Ethanol / Water Mixtures

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Abstract: The stability constant, K_f , for the complexation of copper(II) ion with 4-amino-3-ethyl-1,2,4-triazol-5-thione (AETT) in 0, 20, 40, 60 and 80 (v/v) % ethanol-water mixtures were determined conductometrically at different temperatures. Stability constant of resulting 1:1 complexes were being larger by increasing of temperature and ethanol percent. Stability constants of complexes vary inversely with dielectric constant of solvents. The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constant. In all cases, the complexation were found to be enthalpy unstabilized but entropy stabilized. ΔG^0 of the studied complexes were evaluated at 25°C using thermodynamic relations, the negative values of ΔG^0 means that the complexation process is spontaneously.

Keywords: Complex, Conductometry, Cu(II), Stability constant, Triazole .

Introduction

Copper(II) ion is a biologically active, essential ion, creating ability and positive redox potential allow participation in biological transport reactions. Cu(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and antiinflammatory agents¹. On the other hand, condensed triazoles exhibit a range of pharmacological activities such as mitotic², hypotensive³, CNS stimulant⁴, antiinflammatory^{4,5} and analgesic activities^{6,7}.

The therapeutic effects of 1,2,4-triazole and 1,2,4-triazol-3-one containing compounds have been well studied for a number of pathological conditions including inflammation, cancer, pain, tuberculosis or hypertension⁸⁻¹⁶.

Triazoles fused another heterocyclic ring has attracted wide spread attention due to their application as antibacterial, antidepressant, antiviral, antitumoral and antiinflammatory agents, pesticides, herbicides dyes, lubricant and analytical agents^{17,18}. The present study deals with the conductometric determination of the stability constants, stiochiometric ratio and related thermodynamic parameters of AETT complexes with Cu(II).

Experimental

Reagents

The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ethanol were purchased from Merck. The ligand of AETT was prepared by reported method¹⁹.

Apparatus

Conductivity measurments were carried out with a Metrohm 644 Conductometer. A dip-type conductivity cell, made of platinum black, with a cell constant of 0.69 cm^{-1} was used. In all measurments, the cell was thermostated at the desired temprature $\pm 0.05^\circ\text{C}$ using a ATBIN immersion thermostat.

Procedure

In a typical run, 30 cm^3 of a copper(II) chloride solution ($5 \times 10^{-4} \text{ M}$) was placed in a container having water circulating arrangement. The cell was dipped in the solution. The solution was stirred by using a magnetic stirrer. The desired temperature was maintained by thermostat connected to the water circulating arrangement of the container.

Conductance of the initial solution was measured after thermal equilibrium had been reached. Then a known amount of the ligand solution ($5 \times 10^{-3} \text{ M}$) was added in stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition, and then corrected to avoid the effect of dilution during the titration by multiplying the measured value $[(V + v) / V]$, where V is the original volume of the salt (metal ion solution) and v is the volume of titrant (The ligand solution).

Results and Discussion

In order to evaluate the influence of adding L in the molar conductance of the metal ion used in different ethanol-water (v/v)% mixtures, the conductivity at a constant salt solution ($5 \times 10^{-4} \text{ M}$) was monitored while increasing the L concentration ($5 \times 10^{-3} \text{ M}$) at different tempratures. The molar conductance were plotted against $[L] / [M]$ mole ratio for reaction of Cu(II) with ligand of AETT at different tempratures, as an example, the molar conductance vs $([L] / [M])$ curves for Cu(II)-AETT complexes in ethanol- water 40 (v/v) % at different tempratures is shown in Figure 1. The plots (Figure 1) exhibit one abvious slopes, suggesting that the probable stiochiometric ratio of complexes are M : L. Incidentally, as is expected, the corresponding molar conductance increased with increasing the temprature (Figure 1), owing to decrease viscosity of the solvent and consequently, the enhance mobility of the charged species present in the solution. 1 : 1 Complexes of transition and heary metal ions (M^+) with (L), can be expressed by the following equilibrium²⁰:

The corosponding equilibrium constant, K_f is given by:

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{f_{(ML^+)}}{f_{(M^+)}f_{(L)}} \quad (2)$$

where $[ML^+]$, $[M^+]$, $[L]$ and f represent the equilibrium molar concentration of complexes, free cation, free ligand and the activity coefficient of the species indicated, respectively. Under the dilute condition we used, the activity coefficient of the uncharged ligand, $f_{(L)}$ can be reasonably assumed as unity^{20,21}. The use of Debye-Huckel Limiting Law²² lead to the conclusion that $f_{(M+)} \approx f_{(ML^+)}$, so the activity coefficients in equation 2 were canceled. Thus the complex formation constant in term of the molar conductance can be expressed as Takeda²³, Zollinger *et al*²⁴.

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (3)$$

$$\text{where } [L] = C_L = \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (4)$$

Here, Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal ion, the complex formation constant, K_f , and the molar conductance of complex, Λ_{ML} , were obtained by computer fitting of equation 3 and 4 to molar conductance- mole ratio data using a non linear least- squares program Genplot. All calculated stability constants are summarized in Table 1.

Figure 1. Molar conductance vs $([L]/[M])$ curves for Cu(II)-AETT complexes in 40 (v/v) % ethanol- water binary Mixture at different tempratures

Table 1 shows that stability constant values increase with increasing temprature, *i.e.* the complexation is an endothermic process. Comparison of the formation constants(at identical temprature) given in Table 1 reveals that relative stabilities of the complexes increased with increasing ethanol percent. Since, donor numbers of ethanol(19.0) and water(18.0) are approximately equal^{25,26}, if we ignore negligible difference donor number of solvents, it seems to dielectric constant, ϵ , of solvents^{25,26} play an important role in the formation of complexes.

Stability constants were become large by increasing of ethanol ($\epsilon = 24.3$) percent and decreasing of water ($\epsilon = 81.0$) percent.

Table 1. The stability constant ($\log k_f$) of Cu(II)-AETT complexes in ethanol-water (v/v) % binary mixtures at different temperature.

v/v, % Ethanol-water	$\log K_f$			
	17.5 °C	25.0 °C	35.0 °C	45.0 °C
0	2.43 ± 0.07	2.48 ± 0.07	2.54 ± 0.07	2.60 ± 0.07
20	2.52 ± 0.06	2.57 ± 0.06	2.69 ± 0.07	2.74 ± 0.08
40	2.66 ± 0.07	2.74 ± 0.07	2.81 ± 0.07	2.84 ± 0.07
60	2.71 ± 0.06	2.84 ± 0.07	2.91 ± 0.07	3.00 ± 0.07
80	2.89 ± 0.06	2.95 ± 0.06	3.06 ± 0.06	3.11 ± 0.07

Therefore, stability constants of Cu(II)-AETT complexes vary inversely with dielectric constant of the solvents. In order to have a better understanding of the thermodynamics of complexation reaction discussed, it is useful to consider the enthalpic and the entropic contributions to these reactions. The ΔH^0 and ΔS^0 values for the complexation reaction were evaluated from the corresponding $\ln K_f$ - temperature data by applying a linear least- squares analysis according to the Van't Hoff equation. Plots of $\ln K_f$ vs $1/T$ for Cu(II)-AETT complexes are shown in Figure 2.

Figure 2. $\ln K_f$ vs $1000 / T$ for Cu(II)- AETT complexes in different (v/v) % ethanol – water binary mixtures

The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively. ΔG^0 of the studied complexes were evaluated at 25°C using the relations:

$$\Delta G^0 = -RT \ln K_f = \Delta H^0 - T\Delta S^0 \quad (5)$$

The computed results were collected in Table 2. The negative values of ΔG° (Table 2) show the ability of the studied ligand to form stable complexes and the process trend to proceed spontaneously. However, the obtained positive values of ΔH° (Table 2) means that enthalpy is not the driving force for the formation of the complexes. The positive values of ΔS° (Table 2) indicate that entropy is responsible for the complexing process. For investigating the influence of solvents on the stability constant we draw ($\log K_f$) against (V/V) % of ethanol- water for reaction of Cu(II) with AETT at different temperatures (Figure 3). These plots (Figure 3) were linear, and based of this, can get a result that there is not considerable interaction between components of solvents in binary systems of ethanol-water and this components cause to diluted each other in binary systems.

Table 2. The $-\Delta G^\circ$, ΔH° and ΔS° values for Cu(II)-AETT complexation reactions in different ethanol- water (v/v) % binary mixtures

%, v/ v Ethanol-water	$-\Delta G^\circ$ (25 $^\circ\text{C}$) kcal.mol $^{-1}$	ΔH° , kcal.mole $^{-1}$	ΔS° , cal. mole $^{-1}$. $^\circ\text{K}^{-1}$
0	3.39 ± 0.20	2.65 ± 0.10	20.25 ± 0.34
20	3.52 ± 0.85	3.67 ± 0.33	24.12 ± 1.08
40	3.72 ± 0.77	2.88 ± 0.39	22.13 ± 1.28
60	3.83 ± 0.99	4.38 ± 0.50	27.53 ± 1.63
80	4.03 ± 0.69	3.65 ± 0.30	25.75 ± 0.99

Figure 3. $\log K_f$ vs mole ratio of ethanol for Cu(II)-AETT complexes at different temperatures

Conclusions

The stability constant for the complexation of copper(II) ion with 4-amino-3-ethyl-1,2,4-triazol-5-thione in 0, 20, 40, 60 and 80 ethanol-water (v/v) % mixtures were determined conductometrically at different temperatures. Comparison of the formation constants (at identical temperature) revealed that relative stabilities of the complexes increased with increasing ethanol percent. Thermodynamic parameters of complexation were determined from the temperature dependence of the formation constant. The negative values of ΔG° show the

ability of the studied ligand to form stable complexes and the process trend to proceed spontaneously. However, the obtained positive values of ΔH° means that enthalpy is not the driving force for the formation of the complexes. Furthermore, the positive values of ΔS° indicate that entropy is responsible for the complexing process. The results of this work show that there is not considerable interaction between components of solvents in binary systems of ethanol- water and this components cause to dilute each other in binary systems.

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